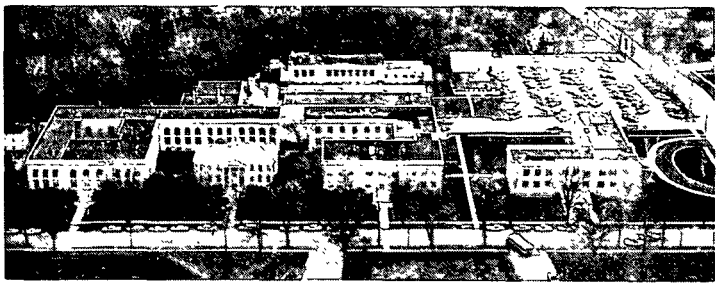

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 66

ACUTE TOXICITY OF BLEACHED KRAFT PULP MILL EFFLUENTS WITH AND WITHOUT ANTHRAQUINONE

E. F. ZANELLA, R. D. McKELVEY, AND T. W. JOYCE

SEPTEMBER, 1978

Acute toxicity of bleached kraft pulp mill effluents with and without anthraquinone

E. F. Zanella, R. D. McKelvey, and T. W. Joyce

ABSTRACT

This work investigates the effects of anthraquinone in bleached kraft pulp mill effluents and their biological treatability and acute toxicity to aquatic organisms. Effluents with and without anthraquinone were treated in laboratory-scale activated sludge reactors. No differences in treatability or effluent characteristics were observed between the two effluents. Samples of effluent after biological treatment with and without anthraquinone were tested on the fathead minnow and *Daphnia* and found to be nontoxic. No difference between survival in the two effluents was observed for the fathead minnow or *Daphnia*.

KEYWORDS: Acute toxicity, Anthraquinone, Bleached kraft, *Daphnia*, Fathead minnow, Activated sludge, Biological treatment, *Pinus taeda*

E. F. Zanella, Research Associate, Bio-Research Group, Environmental Science Division; R. D. McKelvey, Research Associate, Process Research Group, Chemical Sciences Division; T. W. Joyce, Research Fellow, Bio-Research Group, Environmental Science Division.

This paper has been submitted for publication in *Tappi*.

Introduction

In 1972, Bach and Fiehn reported that soluble anthraquinone salts gave increased yields when used as an additive in kraft and soda pulping (1). More recently, Holton (2) and Farrington, et al. (3) independently discovered that anthraquinone itself is a much more effective additive, producing both higher yields and faster rates of pulping. These results have been confirmed by others (4) and the resulting successful mill trials have been reported (5).

Interest in anthraquinone/alkali pulping has become very intense. Due to the minimal capital investment required for implementation, companies are eager to begin using the additive. The immediate application for anthraquinone will probably be modification of the kraft process where it can be used to reduce cooking times, active alkali, and/or sulfidity.

However, in order to be considered a viable and economical improvement, several questions relating to treatability, and possible toxic effects in pulp mill effluents must be considered. If the addition of anthraquinone or its breakdown products require extensive modification of waste treatment facilities or supplementary treatment to reduce toxicity, the economic advantages of increased yield and productivity will be reduced.

This paper describes the differences in the acute toxicity of biologically treated bleached kraft mill effluents with and without the addition of anthraquinone.

Procedures

Effluent Preparation

All work reported in this paper deals with laboratory-scale operations. Both pulping and activated sludge biotreatment of pulping effluents were conducted under lab conditions. Pulping was carried out in multiple 500-ml laboratory pressure vessels which were rotated in a heated oil bath. A 4:1 liquor-to-wood ratio was used with 80 g of oven-dry loblolly pinewood in each vessel. Cooking conditions are given in Table I. Spent liquor was diluted to 4.0 liters during pulp washing. Bleaching was done using chlorination and caustic extraction stages since these would be most likely to contain anthraquinone. Bleaching conditions are given in Table II, and these liquors were diluted during washing to produce effluents.

The feeds to the activated sludge reactors were prepared by mixing 5000 ml black liquor, 7000 ml of chlorine stage effluent, 4000 ml of caustic extraction stage effluent and diluting to 76 liters with tap water. Reagent grade NH_4Cl and KH_2PO_4 were added to provide nutrients. Finally, the pH was adjusted to 7.5 with dilute H_2SO_4.

Simulated final mill effluents were produced by treating the feeds in 3 liter complete-mix activated sludge units. Each reactor was baffled and mechanically stirred to ensure complete mixing. Air was metered through a water filled gas washing bottle to minimize evaporation losses in the reactors. The reactors were fed at a rate of 9 liters/day producing a hydraulic residence time (HRT) of 8 hours. The mean cell residence time (MCRT) was controlled by daily wasting of sludge directly from the reactor. Treatment conditions are given in Table III and discussed later.

The activated sludge units were operated to give conditions typical of those used in full-scale plants. A minimum dissolved oxygen of 2.0 mg/liter was maintained in the reactor while 1.0 mg/liter NH_3-N and 0.5 mg/liter PO_4-P were maintained in the effluent to prevent nutrient limitations.

The reactors were operated until a steady-state condition, as judged by stable effluent quality over time, was reached. Samples were then taken for toxicity analyses.

Toxicity Analyses

Acute toxicity was examined by use of several target organisms and methods. Static assays with the fathead minnow (Pimephales promelas) were conducted in polyethylene bag aquaria (6) at a temperature of 23°C for 96 hours. Toxicity was expressed as a standard LC_{50}, or the concentration at which 50% of the test organisms survived for 96 hours. Two replicate tests were run with 5 effluent concentrations and one control population of 10 fish per concentration for each replicate. Treated effluents to be assayed were collected daily and held in the dark at 4°C until sufficient volumes were available to be tested.

The fathead minnow was also used in a residual oxygen assay (sealed bottle test) similar to that described by Ballard and Oliff (7) and used by Vigers and Maynard (8) as well as McLeay (9). Fish loadings of between 2 and 10 grams per liter in standard 310 ml BOD bottles were used at ambient temperatures which varied between 19-24°C.

Effluents were further tested using laboratory reared cultures of Daphnia magna under static bioassay conditions at ambient temperature

without feeding. Both adults and early instars (less than 24-hr old) were tested for 48 and 96 hours. Twenty individuals were used per concentration with five individuals per container of 100 ml of solution. When the two age groups were compared, 10 adults and 10 early instars made up the complement of twenty test animals per concentration.

Results and Discussion

In the preparation of the test effluents, 0.1% anthraquinone was used to reduce the active alkali by 15% and the sulfidity by 50%. The cooking times were the same and, under these conditions, similar kappa numbers were obtained with and without anthraquinone (Table I).

Although it is true that spent liquor is concentrated and burned in the kraft recovery cycle, some liquor finds its way into the bleach plant as well as the mill effluent through pulp washing. Since anthraquinone is virtually insoluble in water, some of it goes with the pulp to the bleach plant as well. Because chlorination often increases the toxicity of organic compounds, ca. 2% of the black liquor was added back to the washed pulp which was then bleached in two stages. Anthraquinone concentrations were determined for the effluents and are given in Tables IV and V. The feeds to the treatment reactors were prepared by mixing the three unit operation effluents in a ratio reported to be typical for a model mill (10). The characteristics of these unit effluents are shown in Table IV. These values are typical of those found for laboratory scale pulping and bleaching effluents. The combined fractions produced an effluent with characteristics as shown in Table V. Table V also presents the final reactor effluent characteristics which were used for toxicity testing of treated mill effluents.

Throughout the course of this study no significant operational problems were encountered. The biological reactor treating effluent without anthraquinone did show some tendency to foam but the foam could be easily dispersed with Dow Antifoam B. The reactors were assumed to be at steady state following a period of time equal to three times the mean cell residence time, at which point effluent quality was stable. There was essentially no difference in the achievement of a steady state between the kraft effluents with and without anthraquinone. There was also no meaningful difference between the final effluents with respect to BOD_5, TSS and color (see Table IV).

Acute Toxicity

Untreated effluent, with and without anthraquinone, was tested by means of the residual oxygen assay using fathead minnows. This test produces a sensitivity threshold which indicates the point at which the fish begins to be affected by toxicity. This point is determined by plotting dissolved oxygen remaining at the time of death against effluent concentration. In Fig. 1 the resulting curves indicate that the toxicity threshold limit was generally the same for both untreated effluents. Kraft effluent without anthraquinone produced a toxicity threshold of 27% while effluent with anthraquinone reached 23%.

Daphnia magna were also exposed to untreated effluents as adults only. Both effluents were found to be toxic to the test organisms. After 48 hours the concentration of effluent without anthraquinone, at which 50% of the Daphnia died (determined by cessation of swimming), was 42%; after 96 hours this remained at 41%. The effluent with anthraquinone showed 50% survival at a 70% effluent concentration after 48 hours; however, the LC_{50} had fallen to 42% after 96 hours. After 96 hours

Daphnia became weakened and died due to starvation in the controls. Observations at or beyond this point became dubious. It can be concluded that the addition of anthraquinone did not enhance the toxicity of untreated bleached kraft effluent.

The more significant question to be answered by this work pertains to the toxicity of the biotreated effluents containing anthraquinone. It is conceivable that anthraquinone compounds or degradation products with increased toxicity could be created in or remain after waste treatment and result in toxic final effluents.

Both treated kraft effluents were assayed for toxicity using fish and Daphnia in replicate with at least two assays performed per target organism for each of the two effluents. The results are summarized in Table VI for Daphnia magna and 96-hour static fathead minnow assays.

Daphnia magna exhibited survival of 85% or better in 100% effluent for both treated effluents tested. In several instances all organisms survived in all tested concentrations for the 48-hour test period. After 96-hours, survival was significantly better in the higher effluent concentrations than in the controls. In one test of kraft with anthraquinone, survival was 10% in the controls but remained at 100% in 100% effluent. This enhanced survival can be attributed to the presence of biological solids which served as food in the higher concentrations of mill effluent (11). Daphnia were not fed during the test and control populations were held in plain water.

Fathead minnows also maintained 90% survival even after 96 hours in 100% treated kraft effluent both with and without anthraquinone. No

differences in fish behavior or survival were observed for the two effluent treatments during the assay.

As shown in Table VI there was no evidence of acute toxicity to Daphnia magna or to fathead minnows tested under static conditions. There was no difference between treated effluents with or without anthraquinone. Results were similar also for early instar Daphnia and adult Daphnia. While the early instars are considered to be appreciably more sensitive than the adults the treated kraft with anthraquinone supported 100% survival even after 96 hours in 100% effluent.

Residual oxygen assays using fathead minnows supplemented the static assays in demonstrating that there was no acute toxicity threshold apparent for either of the two effluents. There were no appreciable differences in dissolved oxygen remaining following death at tested concentrations for either of the two effluents. This test further verified that both treated effluents were not acutely toxic to fathead minnows.

Conclusions

The use of 0.1% anthraquinone in kraft cooking liquors under laboratory conditions produced a more desirable process with respect to reduced alkali and sulfidity. The effluents produced by pulping and bleaching with anthraquinone were found to have characteristics, following biological treatment, similar to effluents without anthraquinone. When the treated effluents were tested for toxicity, three different tests with two different target organisms demonstrated that both effluents produced similar results and were not acutely toxic. Thus the addition of 0.1% anthraquinone did not affect either treatability or acute toxicity of the kraft pulping wastes.

Literature Cited

1. Bach, B. and Fiehn, G., Zellstoff Papier 21 (1): 3 (1972).

2. Holton, H. H., CPPI Tech. Mtg. (Montreal), Feb. 1976: A107.

3. Farrington, A., Nelson, P. F., and Vanderhoek, N., Appita 31 (2): 119 (1977).

4. Ghosh, K. L., Venkatesh, V., Chin, W. J., and Gratzl, J. S., Tappi 60 (11): 127-31 (1977).

5. Holton, H. H. and Chapman, F. L., Tappi 60 (11): 121-5 (1977).

6. Zanella, E. F. and Rades, D. L., Progressive Fish Culturist 35 (3): 182 (1973).

7. Ballard, J. A. and Oliff, W. D., Water Research 3: 313-3 (1969).

8. Vigers, G. A. and Maynard, A. W., Water Research 11: 343-6 (1977).

9. McLeay, D. J., J. Fish. Board Can. 33 (6): 1303-11 (1976).

10. Environmental Protection Agency, "Development document for interim, final, and proposed effluent limitations guidelines and proposed new source performance standards for the bleached kraft, groundwood, sulfite, soda, deink and nonintegrated paper mills." EPA 440/1-76/047-a, Group I, Phase II, January 1976.

11. Zanella, E. F., Conkey, J. C., and Tesmer, M., Tappi, in press.

I. Pulping conditions for kraft effluents with and without anthraquinone

	Kraft	Kraft/AQ
Anthraquinone, %	0.0	0.1
Active alkali, % as Na_2O	20.0	17.0
Sulfidity, %	28.0	14.0
Temperature, °C	174	174
Time to temperature, min	90	90
Time at temperature, min	75	75
Average yield, %[a]	50.9	52.2
Average kappa number	34	34

[a]Pulp yields include ca. 2% of the black liquor solids as intentional carry over to the chlorination stage.

II. Bleaching conditions for both kraft and kraft/AQ pulps

	Stage I Chlorine	Stage II Caustic Extraction
Chlorine, % on pulp	6.0	0.0
NaOH, % on pulp, as NaOH	0.0	3.0
Consistency	3.0	10.0
Temperature, °C	25	60
Time, min	60-65	60

III. Treatment parameters for activated sludge reactors

	HRT[a], hr	MLSS[b], mg/l	MCRT[a], days	pH
Kraft	8	2670	6.9	7.2
Kraft/AQ	8	2320	7.3	6.8

[a]HRT = hydraulic residence time.

[b]MLSS = mixed liquor suspended solids.

[c]MCRT = mean cell residence time.

IV. Characteristics of unit operation effluents

Component	Kraft				
	BOD_5, mg/l	Color, Pt-Co units	BOD_5, mg/l	Color, Pt-Co units	[AQ] mg/l
Dilute black liquor	4470	20,100	3900	18,700	15
Chlorination effluent	610	1,115	690	980	18
Caustic effluent	500	5,510	465	6,350	0.2

V. Reactor feed and effluent characteristics for kraft and kraft/AQ effluents

	BOD_5, mg/l	SCOD[a], mg/l	[AQ] mg/l	TSS, mg/l	Color, Pt-Co units
Feed					
Kraft	215	--	--	10	1010
Kraft/AQ	220	--	2.7	10	970
Effluent					
Kraft	14	530	--	35	820
Kraft/AQ	12	545	2.2	20	850

[a]SCOD = soluble COD.

VI. Summary of toxicity results for kraft and kraft/AQ effluents

Test organisms	Effluent	Results
Daphnia magna — adults	Treated kraft/AQ	48 hr EC_{50} > 100% effluent 96 hr EC_{50} > 100% effluent
	Treated kraft	48 hr EC_{50} > 100% effluent 96 hr EC_{50} > 100% effluent
Daphnia magna — early instars	Treated kraft/AQ	48 hr EC_{50} > 100% effluent 96 hr EC_{50} > 100% effluent
Fathead minnow	Treated kraft	96 hr LC_{50} > 100% effluent
	Treated kraft/AQ	96 hr LC_{50} > 100% effluent

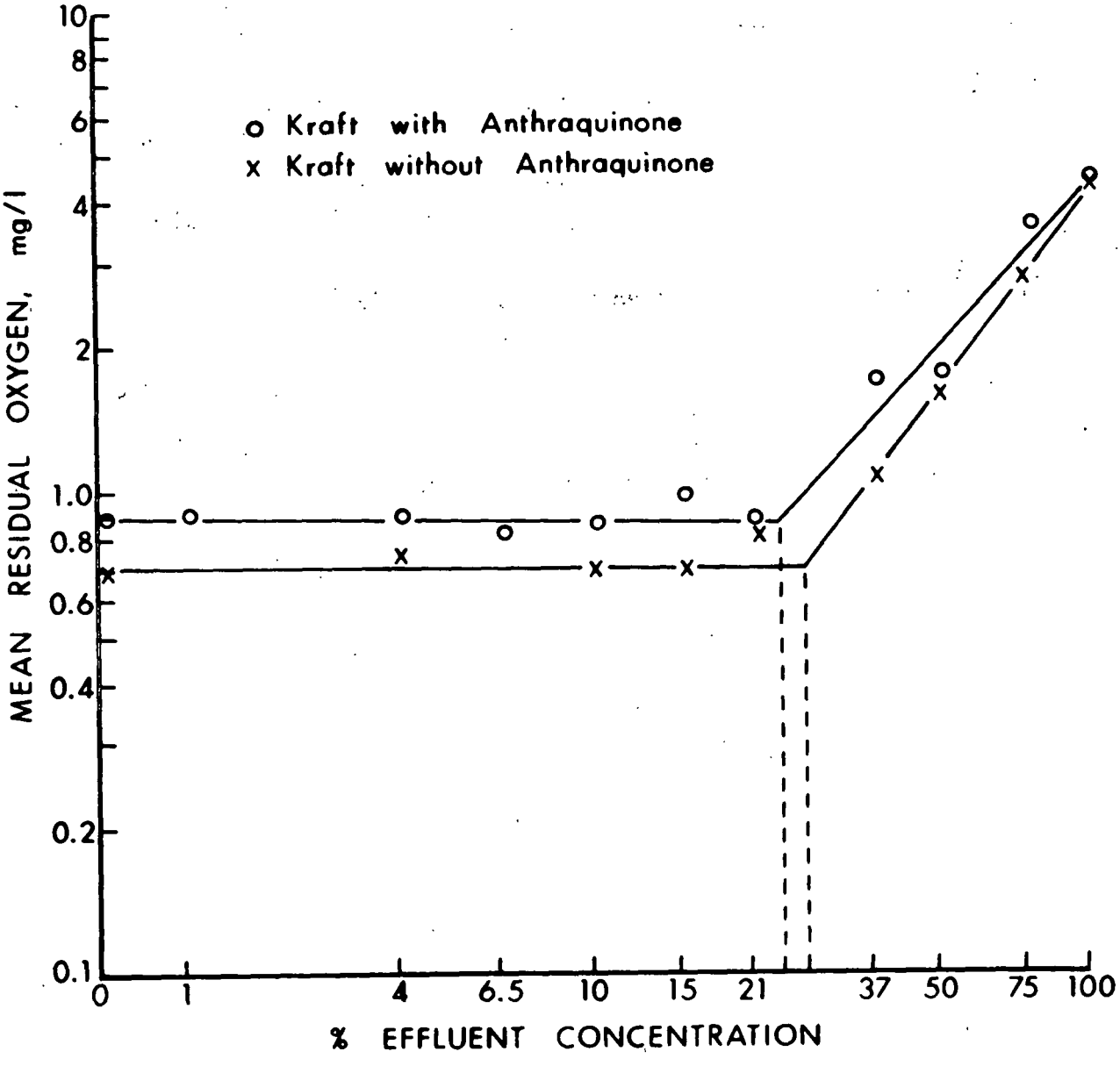

Figure 1. Residual oxygen curves for untreated kraft and kraft with anthraquinone effluents.